Mass Transfer Operations II
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Lecture No. 23
Micellar Enhanced Ultrafiltration

Welcome back to mass transfer operations II, we were discussing on membrane separation processes. Now, we will be discussing the last topic of this mass transfer of a membrane separation processes. That is micellar enhanced ultrafiltration, the name itself suggests that the ultrafiltration process will be enhanced by micelles.

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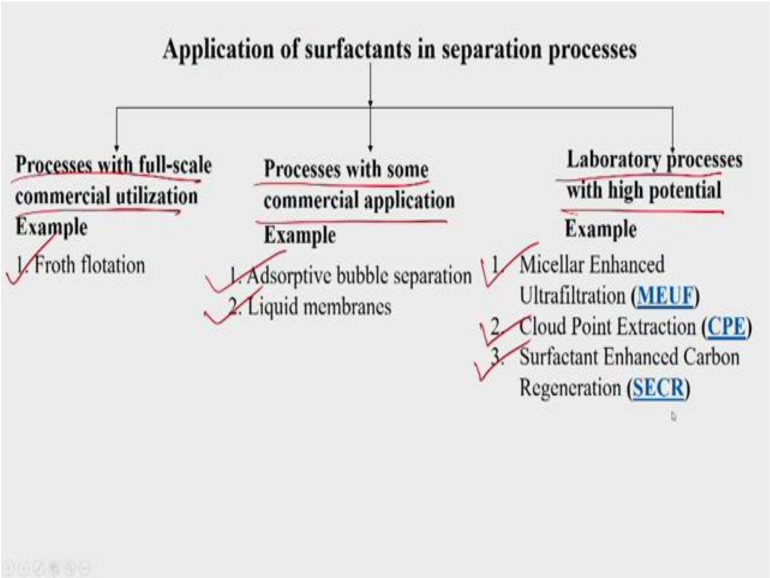

Application of surfactants in separation processes

Processes with full-scale commercial utilization
Example
1. Froth flotation

Processes with some commercial application
Example
1. Adsorptive bubble separation
2. Liquid membranes

Laboratory processes with high potential
Example
1. Micellar Enhanced Ultrafiltration (**MEUF**)
2. Cloud Point Extraction (**CPE**)
3. Surfactant Enhanced Carbon Regeneration (**SECR**)

So, micelles are actually formed using surfactants. So, now we will be discussing about how, surfactants will be enhancing the separation process for ultrafiltration process operation. So, before that we need to learn something about the fabrication of surfactants in separation processes. Like as if we talk about the processes with full scale commercial utilization so, that is we can say froth floatation is there. So, there are like adsorptive bubble separation or liquid membranes are there. And, whenever will be talking about this laboratory processes with high potential, the first is the micellar enhanced ultrafiltration. And, in brief it is a MUEF then we have this cloud point extraction CPE then we have surfactant enhanced carbon regeneration SECR.

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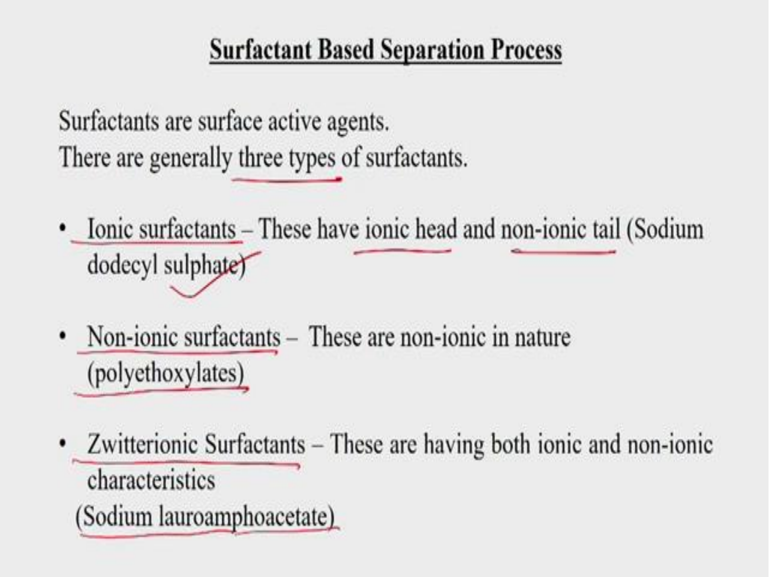

Surfactant Based Separation Process

Surfactants are surface active agents.
There are generally three types of surfactants.

- Ionic surfactants – These have ionic head and non-ionic tail (Sodium dodecyl sulphate)
- Non-ionic surfactants – These are non-ionic in nature (polyethoxylates)
- Zwitterionic Surfactants – These are having both ionic and non-ionic characteristics (Sodium lauroamphoacetate)

So, now we will be discussing about the surfactant based separation processes in detail. So, before that we need to understand the meaning of this surfactant or we can say these surfactants are surface active agents. There are generally 3 different types of surfactants, like ionic surfactants are there. Maybe say we can say this ionic head and nonionic tail will be there. Example, is suppose this SDS sodium dodecyl sulphate or cetyl pyridinium chloride or so many.

And, then we have this nonionic surfactants, these are nonionic in nature like say polyethoxylates. Then third type is say zwitter-ionic surfactants. We can say these are having both ionic and nonionic characteristics. Like we can say sodium lauroamphoacetate like so and there are so many we can say ionic surfactants nonionic surfactants and zwitter-ionic surfactants. Many surfactants are also edible in nature.

In so many food grade products also some ionic surfactants are also used to stabilize the say food grade products or to preserve for a long period of time. But, here we will be discussing about the any separation process which is related to surfactants. And, especially in ultrafiltration process we will be discussing the role of this different surfactants both ionic means cationic or anionic surfactants. Or we can say both cationic and anionic in a whole say how these are contributing towards the separation in the ultrafiltration process.

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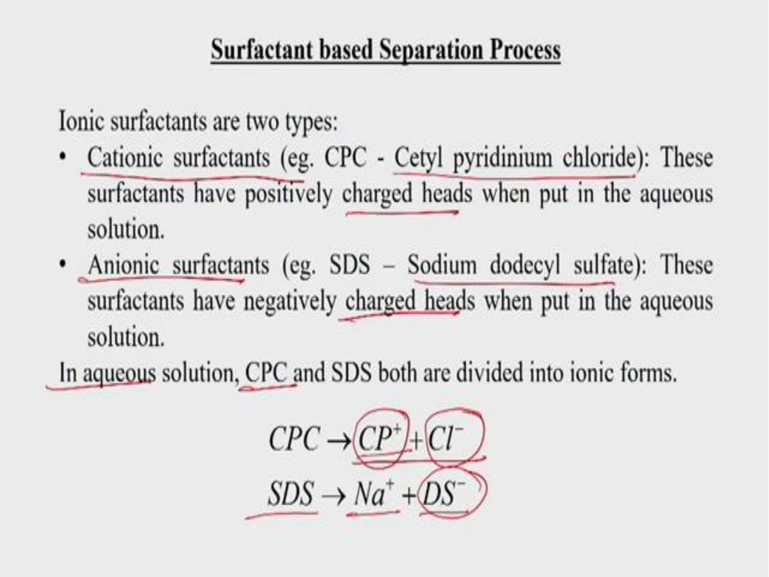

Surfactant based Separation Process

Ionic surfactants are two types:

- Cationic surfactants (eg. CPC - Cetyl pyridinium chloride): These surfactants have positively charged heads when put in the aqueous solution.
- Anionic surfactants (eg. SDS – Sodium dodecyl sulfate): These surfactants have negatively charged heads when put in the aqueous solution.

In aqueous solution, CPC and SDS both are divided into ionic forms.

$$CPC \rightarrow CP^{+} + Cl^{-}$$

$$SDS \rightarrow Na^{+} + DS^{-}$$

So, the anionic surfactants are of 2 types as told this previously that suppose cationic surfactants cetyl pyridinium chloride. Where we can say these one chloride is minus and then cetyl pyridinium is the cationic part. So, these surfactants have positive charged heads. When put in the aqueous solution so, negatively charged particles will be attracted by this positively charged heads. For anionic surfactants like say sodium dodecyl sulfate these surfactants have negatively charged heads so when it is put in the aqueous solution.

So, if we want to separate this we can say positively charged particles. Then we shall go for this anionic surfactant mediated ultrafiltration process. In aqueous solutions we can say the CPC that we can say cationic surfactant will be separated into CP plus cetyl pyridinium plus and chloride minus. This CP plus actually cetyl pyridinium plus will attract this negatively charged solutes. For SDS say it will be dodecyl sulphate part will be minus and Na plus will be there. So, this dodecyl sulphate part will attract the positively charged particles from aqueous solution.

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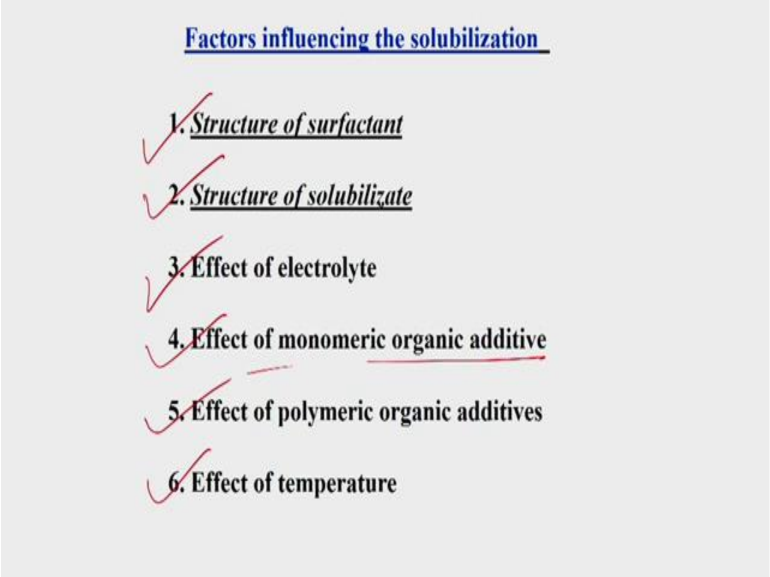

Factors influencing the solubilization

1. *Structure of surfactant*
2. *Structure of solubilizate*
3. Effect of electrolyte
4. Effect of monomeric organic additive
5. Effect of polymeric organic additives
6. Effect of temperature

Now, we need to understand the factors that influence the solubilization of the charged particle or the particles which will be separated using the surfactant mediated separation processes. The first factor is this structure of the surfactant. So, till now we have learnt that the types of surfactants are of like ionic surfactants then nonionic surfactants and zwitterionic. Say in ionic we have cationic and anionic. So, what type of structure of the surfactant is there? Or if it is a cationic surfactant, what is the bulkiness of the cationic part or what is bulkiness of the anionic part of the anionic surfactant?

Or whenever the surfactant will make the micelles or will make the globule. Say above the critical wisely concentration will be discussing detail about that. So, what type of shape actually it will create? So that controls the solubulization of the solute particle or, separation of particular target component using the surfactant. Then structure of the solubilizate or target component.

What is the structure of the target component? Then the structure of the target component or solubilizate would be opposite in nature or top surface would be oppositely charged so that this will be coming closer or in contact due to the electrostatic force of attraction. Then third factor is the effect of electrolyte so in his electrolytic solution the target component or solubilizate is there and also the surfactant actually is added inside this electrolyte.

So, depending on the polarity of the electrolytes we can say the separation or we can say this stabilization of the target component, as well as this surfactant will take place and accordingly the separation will take place. Then effect of monomeric organic additive so that is also required in some surfactant mediated separation processes, some monomeric organic additive also are added. This will say trap this target component and this will it will try to help to be trapped by the surfactant this one with the help of that additive.

Like this, then the effect of this polymeric organic additive is also there. And, then effect of temperature so if the process is endothermic in nature, say with addition of temperature the process will be very forward. If the process is very exothermic, then we can say at the lowering the temperature the process will be favorable.

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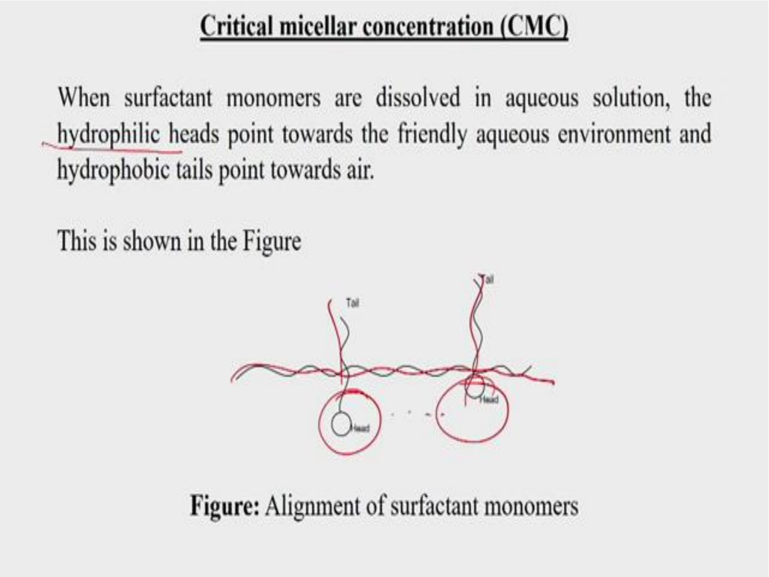

Critical micellar concentration (CMC)

When surfactant monomers are dissolved in aqueous solution, the hydrophilic heads point towards the friendly aqueous environment and hydrophobic tails point towards air.

This is shown in the Figure

Figure: Alignment of surfactant monomers

Now, we need to understand the meaning of this critical micellar concentration. Because, we see for micellar enhanced ultrafiltration or surfactant mediated separation processes we need to understand the concentration of the surfactant, above or below the CMC or critical micellar concentration. So, when surfactant monomers are dissolved in aqueous solution. The hydrophilic heads actually point towards the friendly aqueous solution, suppose this is the aqueous solution like this. So, we can say this hydrophilic heads are all heading or pointing towards the friendly aqueous environment and hydrophobic tails actually will be towards the air. So, hydrophobic tails will be, we can say spread towards the air like this.

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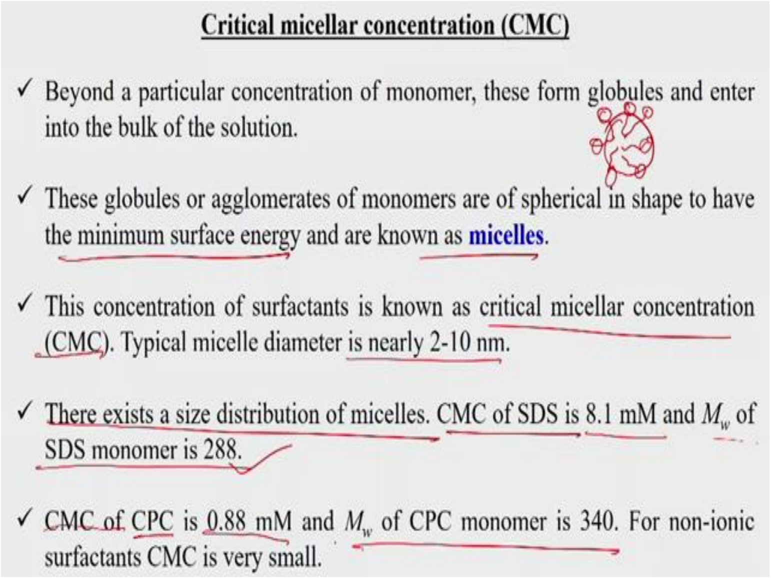

Critical micellar concentration (CMC)

- ✓ Beyond a particular concentration of monomer, these form globules and enter into the bulk of the solution.
- ✓ These globules or agglomerates of monomers are of spherical in shape to have the minimum surface energy and are known as **micelles**.
- ✓ This concentration of surfactants is known as critical micellar concentration (CMC). Typical micelle diameter is nearly 2-10 nm.
- ✓ There exists a size distribution of micelles. CMC of SDS is 8.1 mM and M_w of SDS monomer is 288.
- ✓ CMC of CPC is 0.88 mM and M_w of CPC monomer is 340. For non-ionic surfactants CMC is very small.

So, when beyond a particular concentration of the monomer this form the globules and enter into the bulk of the solution. So, one globule will be formed where we can say this way say hydrophobic tails actually will be concentrating inside this aqueous solution only to be stabilized. So, it will make a sphere so, this globules or agglomerates of the monomers are of spherical in shape to have the minimum surface energy.

Because, in that case only as the surfactant dissolve in aqueous solution. So, 2 have minimum surface energy. So, it will try to be this one stay in the globular form or it can be in a spherical form. So, this sphere actually is called micelles. So, the so many micelles actually will be formed when the surfactants will be dissolved above the with their typical micellar concentration.

So, this concentration of the surfactant is known as the critical micellar concentration then in brief it is called CMC. The typical micellar diameter varies from 2 to 10 nanometer depending on the bulkiness of the surfactant we can say bodies. There exists a size distribution of micelles so it is not allows the size of the sphere will be uniform. So, this may be varying in a wide range. So, the CMC of the sodium dodecyl sulphate is 8.1 millimolar and molecular weight of the SDS is 288. Whereas, the CMC of this cetyle pyridinium chloride is 0.88 mM, this is very almost ten times lower than SDS. And, molecular weight CPC monomer is 340 for nonionic surfactants the CMC is very small.

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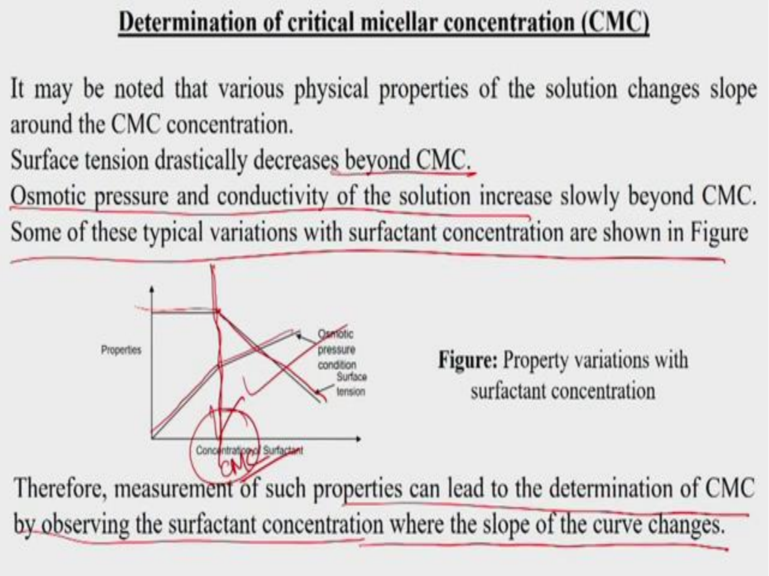

Determination of critical micellar concentration (CMC)

It may be noted that various physical properties of the solution changes slope around the CMC concentration.

Surface tension drastically decreases beyond CMC.

Osmotic pressure and conductivity of the solution increase slowly beyond CMC.

Some of these typical variations with surfactant concentration are shown in Figure

Figure: Property variations with surfactant concentration

Therefore, measurement of such properties can lead to the determination of CMC by observing the surfactant concentration where the slope of the curve changes.

Now, we need to learn how to determine the critical micellar concentration. So, whenever we have the monomers in the dissolved form in the aqueous solution then this will try to be accommodated in a spherical shape. And, then the minimum surface energy will be obtained. And, that is why say the physical properties of the micelles will be changing drastically when it is in monomer. And when it will be converting into the we can say micelle. So, it may be noted that various properties means the physical properties of the solution changes around the CMC concentration.

And, surface tension drastically decreases actually beyond the CMC level. Osmotic pressure and conductivity of the solution increase slowly beyond CMC. So, some of these typical variations with surfactants concentrations are shown in this figure. Like we can say this surface tension values will be remain almost in variant and when it will be forming the micelle. Then drastically the surface tension value will go on decreasing. So, because that time the so many surfactants actually monomers will be agglomerated like this osmotic pressure also.

It will be increasing slowly and slowly and once it exceeds its CMC value, then the osmatic pressure value will not increase drastically. And, there are so many parameters so there is one concentration beyond this. So, all the properties will behave differently from the properties below this concentration. The particular concentration is CMC critical micellar concentration. Or when the micelles will be formed inside this aqueous solution their physical properties will changed drastically.

So, therefore measurement of such properties can lead to the determination of CMC by observing the surface surfactant concentration where the slope of the curve changes. So, the particular concentration of the surfactant is termed as the critical micellar concentration. And, if we want to use this concept to separate the solute particles from the bulk with the help of this membrane, then, our surfactant concentration should be well above this CMC.

So, that the monomers will be forming globules and then the globules will be attracting the solutes. And, then with the help of this bigger pore diameter containing membranes we will be able to trap the small diameter solutes. And, that is the beauty of the micellar enhanced ultrafiltration process. Means, the molecules with the nanometer range will be separated by ultrafiltration membranes that is why the through put will be very high.

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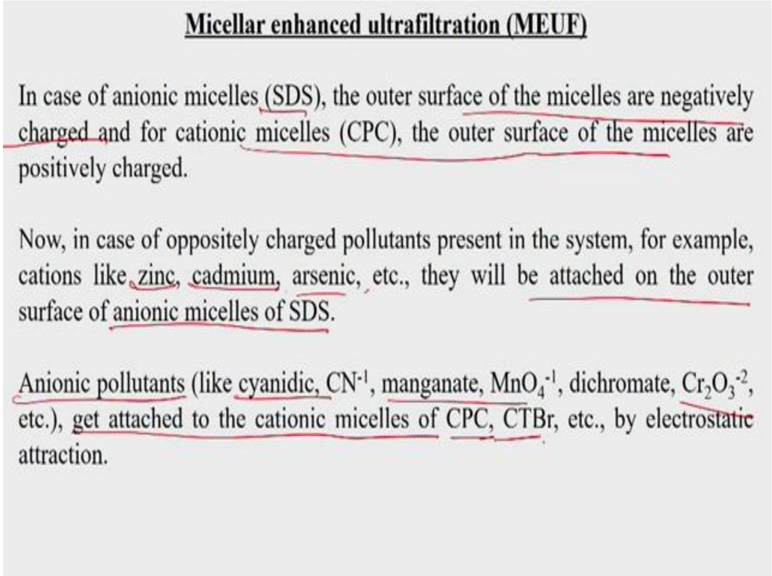

Micellar enhanced ultrafiltration (MEUF)

In case of anionic micelles (SDS), the outer surface of the micelles are negatively charged and for cationic micelles (CPC), the outer surface of the micelles are positively charged.

Now, in case of oppositely charged pollutants present in the system, for example, cations like zinc, cadmium, arsenic, etc., they will be attached on the outer surface of anionic micelles of SDS.

Anionic pollutants (like cyanidic, CN^{-1}, manganate, MnO_4^{-1}, dichromate, $Cr_2O_3^{-2}$, etc.), get attached to the cationic micelles of CPC, CTBr, etc., by electrostatic attraction.

Now, whenever will be discussing about the micellar enhanced ultrafiltration. So, in this case of anionic micelles like sodium dodecyl sulphate the outer surface of the micellar negatively charged. So, because that is why it is an anionic surfactant. And, for cationic micelles we can say the outer surface of the micelles are the positively charged. Now, in case of the oppositely charged pollutants presents in the system for example we can say the cations like zinc plus 2 plus and then cadmium 2 plus or arsenic three plus etc.

They will be attached on the outer surface of anionic micelles of the SDS. So, we will be preferring this SDS to separate the metal ions. Because, this are anionic surfactants the top surface of the micelles will be again negatively charged. Where the metal ions will be of the positively charged then due to this electrostatic force of attraction. The metal ions will be attached on the top surface of the micelles and this will not pass through the highly pores ultrafiltration membrane.

If we do not use this micelles surfactants or, if we do not use the micelles. Then, all the metals actually will be passing through the ultrafiltration membrane. And for anionic pollutants like we can say cyanidic or magnate or we can say the dichromate or any other anionic we can say pollutants. These will be attached to the cationic micelles of cetyle pyridium chloride or cetyl this one triisobenzyl bromide or so many other anionic surfactants by only electrostatic force of attraction.

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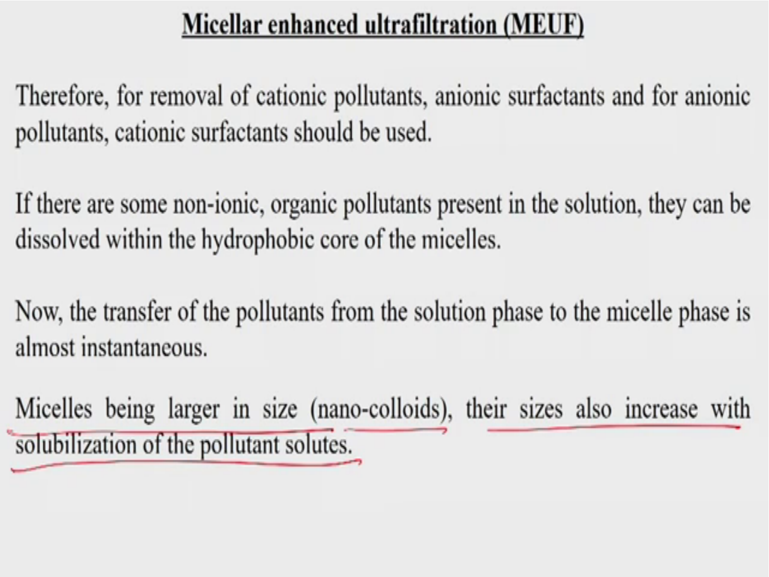

Micellar enhanced ultrafiltration (MEUF)

Therefore, for removal of cationic pollutants, anionic surfactants and for anionic pollutants, cationic surfactants should be used.

If there are some non-ionic, organic pollutants present in the solution, they can be dissolved within the hydrophobic core of the micelles.

Now, the transfer of the pollutants from the solution phase to the micelle phase is almost instantaneous.

Micelles being larger in size (nano-colloids), their sizes also increase with solubilization of the pollutant solutes.

So, therefore for removal of cationic pollutants the anionic surfactants are required for anionic pollutants cationic surfactants are used. If there are some nonionic or organic pollutants present in the solution. They can be dissolved within the hydrophobic core of the micelles so that will be discussing also latter on. So, if we have some nonionic or organic pollutants, or some pollutants with the slightly delta positive or delta negative charged on the top surface this will be we can say dissolve inside the core of the micelles.

Only due to the presence of the inter molecular space inside the globules. So, now the transfer of the pollutants from the solution phase to the micelle which is almost instantaneous. Because, the concentration of the solute inside micelle is 0. Where, the concentration of the solute in the bulk is in concentration at the concentration of the solute concentration of the bulk. So, due to this CB minus say C micelle. That is actually driving force is entirely the concentration gradient or whatever the solute concentration is present in the bulk.

So, due to that the pollutants will be transferring instantaneously when the solutions surfactants solution above CMC will be dissolved. But, one point actually we need to mention here that, if the surfactant also is above the CMC values some monomers also will be present on we can say surfactant solutions. So, micelles being larger in size like this nano colloids. Their sizes also increase with solubilization of the pollutants or whenever the pollutant will be attached at the top surface due this electrostatic force of attraction.

The size of the micelle will go on increasing at the same time. If, the solutes are dissolved or solubilized inside the core of the micelles also then the size of the micelles also will go on increasing. And, the one time we will reach when we can say that it will exceed it with a capacity limit. Then the micelles will not able to separate the particular we can say this ionic or nonionic or organic pollutants. Using these surfactants mediated separation processes or micellar enhanced ultrafiltration process.

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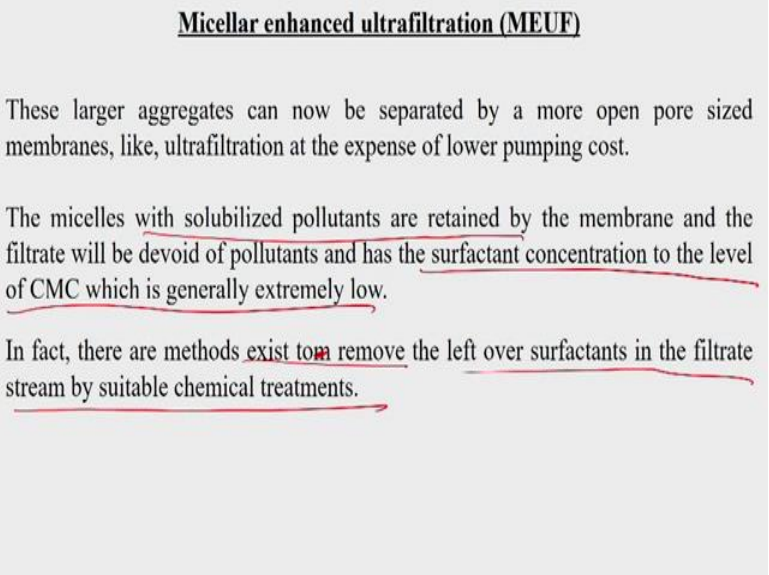

Micellar enhanced ultrafiltration (MEUF)

These larger aggregates can now be separated by a more open pore sized membranes, like, ultrafiltration at the expense of lower pumping cost.

The micelles with solubilized pollutants are retained by the membrane and the filtrate will be devoid of pollutants and has the surfactant concentration to the level of CMC which is generally extremely low.

In fact, there are methods exist to~~m~~ remove the left over surfactants in the filtrate stream by suitable chemical treatments.

So, this large agglomerates can now be separated by a more open pore sized membranes like this ultrafiltration at the expense of low pumping cost. So, these metal ions which were able to separate by either this reverse osmosis membrane or nano filtration membrane. Now, will be this one will be able to separate using this highly pores ultrafiltration membranes. Because, the micelles will attract the metal ions and then micelles will not be allowed to pass through pore of the ultrafiltration membrane.

The micelles with the solubilized pollutants are retained by the membranes and the filtrate will be devoid of the pollutants. And has the surfactant concentration to the level of CMC which is generally extremely low. So, as the CMC or critical micellar concentration of the surfactants are always very low. So, at the lower concentration though surfactant will be able to separate the ionic particles especially suppose metal ions or any anionic part like permanganate or dichromates cyanide or cyanates, etc. with the expense of a small amount of surfactant.

So, in fact there are methods exist to remove the left over surfactant in the filtrate stream by suitable chemical treatment. We will be discussing also the beauty of the surfactant mediated separation process is that once, the process is over. Whatever the surfactants actually will be coming out through this retentate or permeate will be recover and that can be used as again for the same process.

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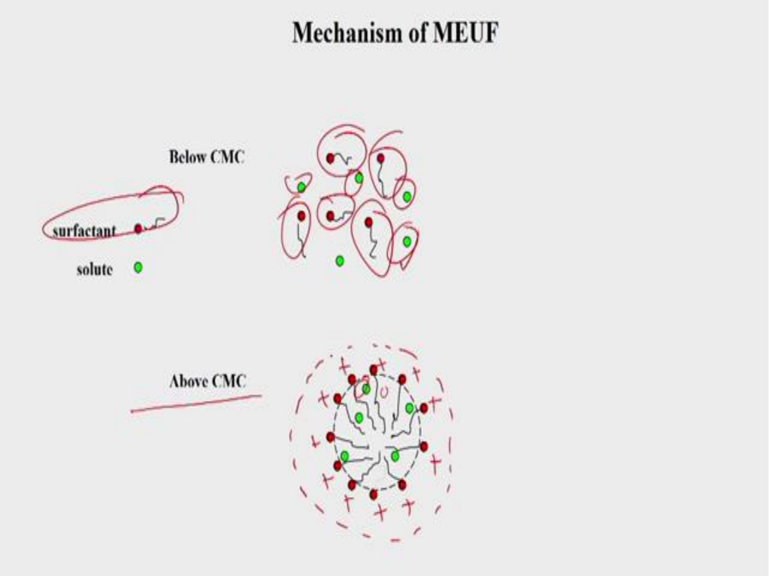

Mechanism of MEUF

Like this is mechanism of a MEUF like this below CMC value suppose surfactants are all this are in the monomeric form. So, it is not able to attract so many solutes very easily. But, whenever it is above CMC then you see the solutes are trapped inside this one. And, if we say if we say if it is like positively charged the globules are in the positively charged. Then, say negatively charged will be say we can this attached from the top of this one or the reversal will be if the surfactant is negatively charged. We can say anionic surfactants then cations will be attracted and it will form a layer this above the anionic surfactant.

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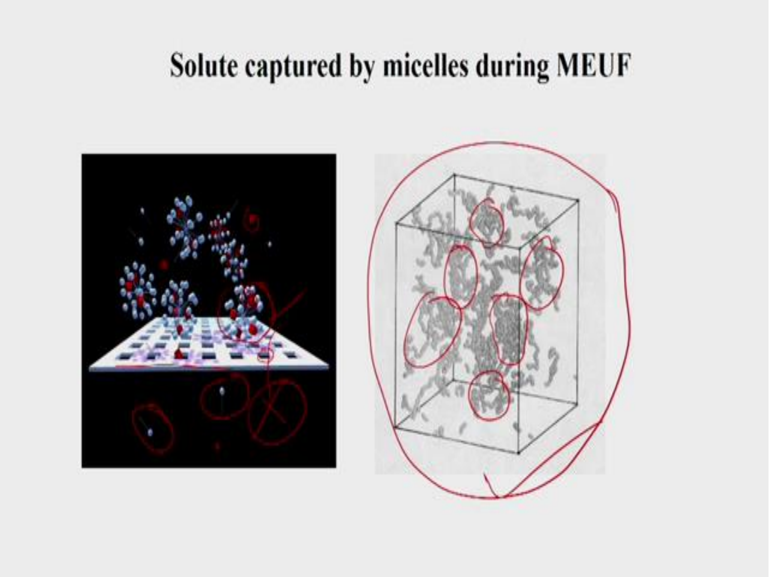

Solute captured by micelles during MEUF

And, now you see this one suppose the solutes are now trapped inside this we can say CMC we can say these micelles suppose the solutes are trapped. Now, this is the membrane big pores. But, if you remember this one the pores of this ultrafiltration membrane much more higher than the size of the solute. But, due to this electrostatic force of attraction of this micelles, the solute which will not pass through this one that is why this solute passage is not present here.

But you see I mentioned earlier also that some monomers actually of the surfactants will be passing through this membrane. But, that is very negligible and we will be discussing that this will be separated very easily. And, this is the image of the micellar ultrafiltration this are micellar of the surfactants and this are able to trapped to either cationic anionic or nonionic or pore organic pollutants this one efficiently.

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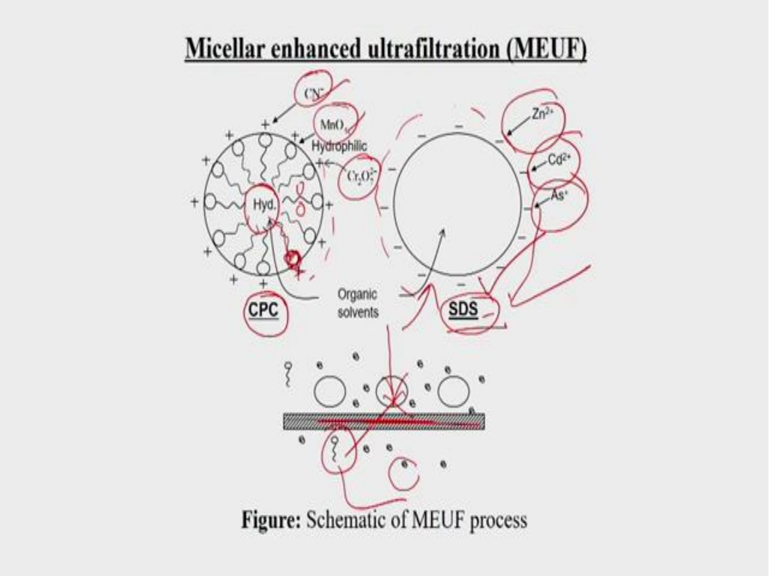

Micellar enhanced ultrafiltration (MEUF)

Figure: Schematic of MEUF process

Now, this is like say cetyl pyridinium chloride that is the positively cationic surfactant and this is sodium dodecyl surfactant that is we can say anionic surfactant. So, you see this we can say this hydrophilic heads are now their tails are there, concentrating inside this globule and then hydrophilic heads are heading towards the outer surface of the micelles. So, it can attract so many cationic anionic pollutants like this chromate or manganite or cyanate, etc.

And at the top surface like this and which are nonionic in nature this will be trapped inside the sodium dodecyl sulphate, say mental ions will be attracted on the top surface of the SDS globule. So, whenever we will be talking about the membrane the pores are very big but, you say due to this attraction of the charged particles with the surfactant micelles this will be you will not be passing through this one.

So only some monomers will be passing and that is why the efficiency of the micellar enhanced ultrafiltration is much higher than any say ultrafiltration process even the nano filtration process also of the same solute.

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MEUF using cationic surfactant

Now, we will be discussing 3 different cases say one will be like MEUF using cationic surfactant. Then will be discussing of the MEUF using anionic surfactant. And third one we will be discussing MEUF using this both cationic and anionic surfactants. So, mixed surfactant will be using to separate the different cationic anionic parts. Firstly, we will be using about the MEUF using this cationic surfactants.

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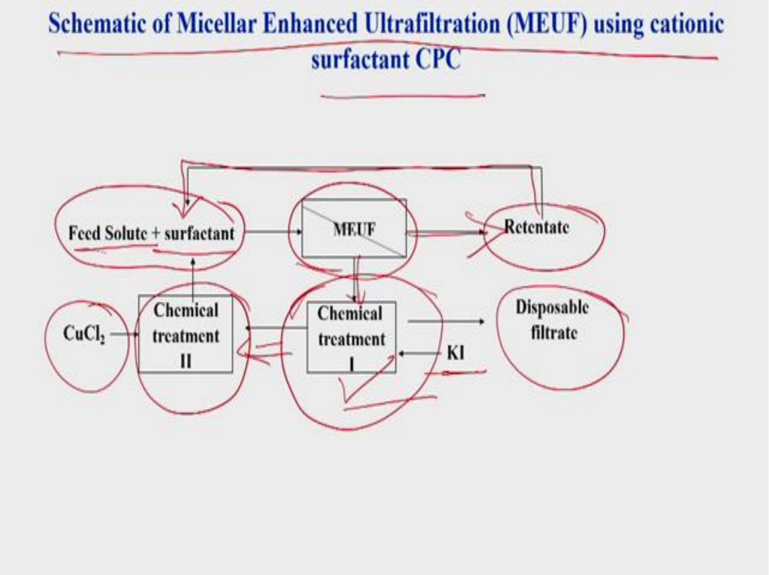

Schematic of Micellar Enhanced Ultrafiltration (MEUF) using cationic surfactant CPC

Feed Solute + surfactant

MEUF

Retentate

$CuCl_2$

Chemical treatment II

Chemical treatment I

KI

Disposable filtrate

So, this is the schematic of the MEUF process using this cationic surfactant. Suppose, feed solute is there inside this aqueous solution and we have added the surfactant above CMC value. Then the edge we discussed earlier that the feed solutes will be attracted by these cationic surfactants. Then we will be using this MEUF process then we have 2 different parts

1 is the retentate another one is this permeate. This retentate will be with more the surfactants because you see as we have added above CMC.

So, it is presumed that the most of the monomers are now converted into the bulk this one above this micelles concentration though they formed the micelles. So, the micelles will be there with the retentate. And, then we need to use this one again with some treatment or without treatment also. But, whatever the permeate actually we are getting may be it may contain some amount of the surfactant. Along with my minimum amount of the target component or solute.

So, we will be going to for this first chemical treatment one with the help of potassium iodate. And, then we will be first will be trapping these monomers or if the some micelles are there this will be trapped potassium iodate. And, then we will be regenerating in the chemical reaction two skin using copper chloride to give this again cetyl pyridinium chloride we will be discussing this one. And, during this chemical treatment process one using this potassium iodate. Whatever the filtrate actually disposable filtrate will be there we need to discard this and we will be discussing this later on.

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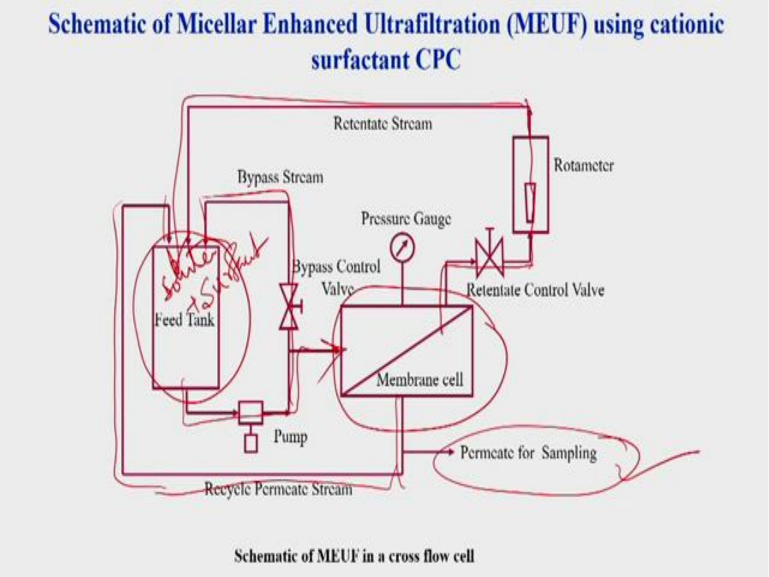

Schematic of Micellar Enhanced Ultrafiltration (MEUF) using cationic surfactant CPC

Schematic of MEUF in a cross flow cell

Say like this is the membrane cell and we have this feed tank inside this feed suppose we have the solute and we have surfactant say cationic surfactant we have. Suppose, if we say CPC is there or surfactant is there. Then, through this pump it will enter into the membrane cell then from the retentate line the solute globules of the surfactant will again come back to the figure feed tank. But, whatever the permeate actually be coming out some portion will be going for sampling and some portion will be recycled actually after this treatment. But the bypass line is there to control the flowrate through this membrane cell.

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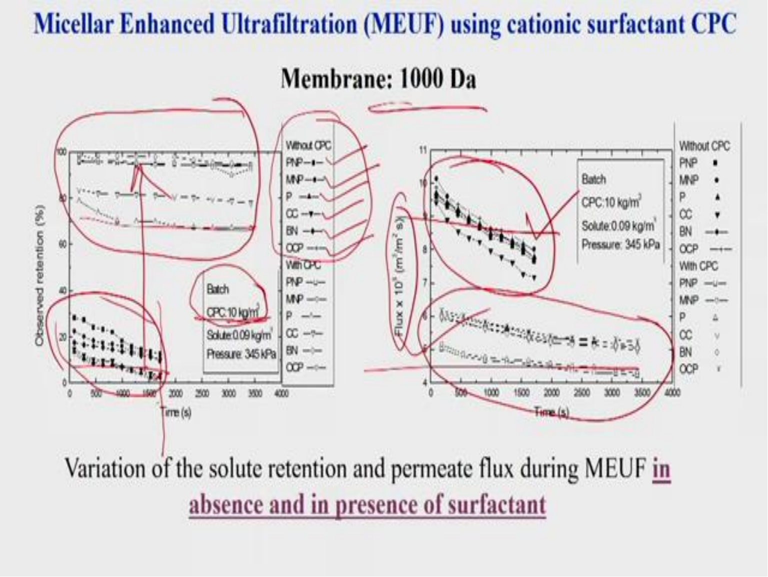

Micellar Enhanced Ultrafiltration (MEUF) using cationic surfactant CPC

Membrane: 1000 Da

Variation of the solute retention and permeate flux during MEUF in absence and in presence of surfactant

Now, this is a typical example of the micellar enhanced ultrafiltration process using the cationic surfactant. The example this figure actually is given here only to make us understand that. Whenever we have this any for any batch process suppose the surfactant concentration of cetyl pyridinium chloride is 10 kg per meter cube so, that is above the CMC value. So then you see for the some pollutants like paranitrophenol or metanitrophenol then phenol catechol, beta naphthol, ortho chlorophenol

So, all this case whenever we have this without the any surfactant there you see observe retention values are always less than 30 percent. It indicates that the size of the all the organic compounds are so small. That through this 1000 Dalton membrane that is the ultrafiltration membrane. All the solutes are passing almost all the solutes are passing means only rejection that is maximum 30 percent. But, after say 1750 second the most of the cases you see the observe retention values goes beyond 7 or 8 percent.

So, all this are permeating through the membrane. Because, it is obvious thing that the size of all the organic compounds are below 350 or like this. So, that is why this are not written on the membrane surface. But, once 110 kg per meter cube CPC cetyl pyridinium chloride is added to all off this suppose this all the organic pollutants. Then you say the retention values are now shooting up to say from 7 percent around say in some cases it is almost 98.9 percent.

Whereas, for few cases only it is almost up to 70 percent. So, from 7 percent to 95 or 96 percent retention value increase is only due to formation of the micelles of the cetyl pyridinium chloride. And, it is a cationic surfactant and that is why all this organic compounds are now trapped on the surfactant micelles. But, one point is that say whenever will be talking about the permeate flux values or throughput of the process then the trend is reversed. Whenever we have this only pure organic compounds, their permeate flux values are very high.

Because, there is no globule or there is no resistance but, whenever the surfactant is added then flux values are decreased. But, here if we compare this we can say rejection with this flux values then rejection values were more than 10 or 15 times. Whereas the flux values are decreasing by only 2 times. Means, say this whenever we will be adding surfactant then flux values will be decreasing. Suppose, form 9 meter cube per meter square second into 10 to the power minus 6 to it is coming out at around say 4 or like this.

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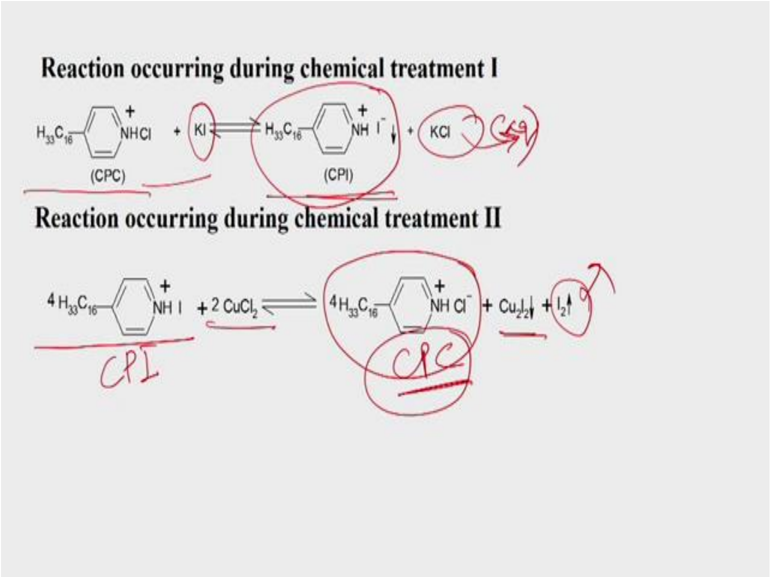
Chemical treatment for recycling of surfactant



Reaction occurring during chemical treatment I

Reaction occurring during chemical treatment II

So, now the one important point or we say beauty of this micellar enhanced process that we can recover the surfactant from both the permeate and retentate and this will be reused for the system. So, the first treatment process we whatever we mention from the permeate like this we need to add the potassium iodide. Because suppose CTM cetyl pyridinium chloride was there in the permeate either in the monomeric form or in the globule form.

When it will be reacting with potassium iodate then it will be forming this cetyl pyridinium iodate that will be precipitated out and then potassium chloride will there in the aqueous solution. Now, whatever the precipitated actually we have citium, cetyl cetyl pyridinium iodide we now we need to add copper chloride to get back this CPC. So, that CPC is nothing but the CPC what we used for the previous separation process. And, copper chloride will be precipitated out and iodine will be liberated. So, this whatever the CPC will be will be generating from the second chemical treatment process that will be again used for the next micellar enhanced ultrafiltration process. And we have observed that above 90 percent surfactants where recovered using this reaction, two reactions in chemical treatment process I and followed by chemical treatment process II.

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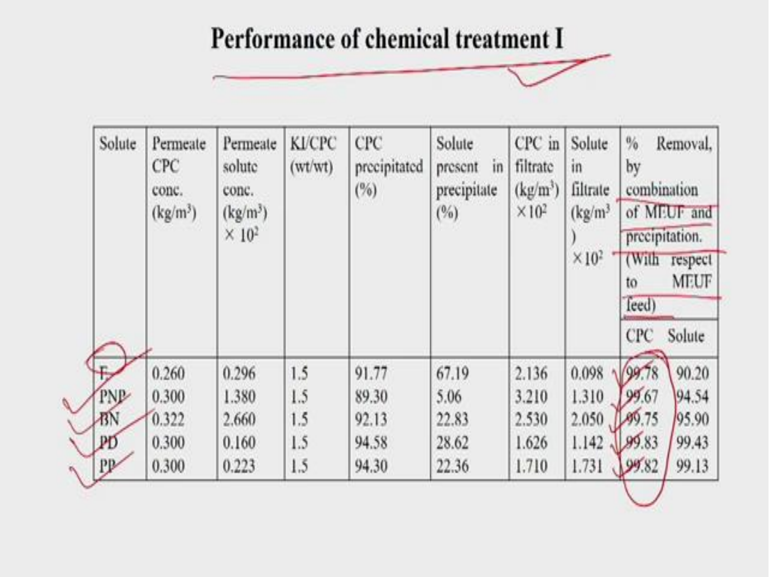

Performance of chemical treatment I

Solute	Permeate CPC conc. (kg/m^3)	Permeate solute conc. (kg/m^3) × 10^2	KI/CPC (wt/wt)	CPC precipitated (%)	Solute present in precipitate (%)	CPC in filtrate (kg/m^3) ×10^2	Solute in filtrate (kg/m^3) ×10^2	% Removal, by combination of MEUF and precipitation. (With respect to MEUF feed)	
								CPC	Solute
E	0.260	0.296	1.5	91.77	67.19	2.136	0.098	99.78	90.20
PNP	0.300	1.380	1.5	89.30	5.06	3.210	1.310	99.67	94.54
BN	0.322	2.660	1.5	92.13	22.83	2.530	2.050	99.75	95.90
PD	0.300	0.160	1.5	94.58	28.62	1.626	1.142	99.83	99.43
PP	0.300	0.223	1.5	94.30	22.36	1.710	1.731	99.82	99.13

This is whatever we discussed like this for chemical treatment process I you see the CPC recovery was more than 99 percent in all the cases, whenever we have, we can say eosin, paranitrophenol, beta naphthol, potassium dichromate, potassium permanganate like this. For all the cases you see percentage removal by combination of MEUF and precipitation like this one with respect to MEUF feed. So, the CPC recovery was like this above 99 percent.

So, in this case whenever CPC is used for the separation of organic pollutants then the recovery of the CPC from the permeate is above 99.9 percent. So, we can say this almost 100 percent CPC is recovered and it is observed that the usage of this recover surfactant is feasible and the properties of this surfactants are similar to that of the pure surfactant as well as the recover surfactant.

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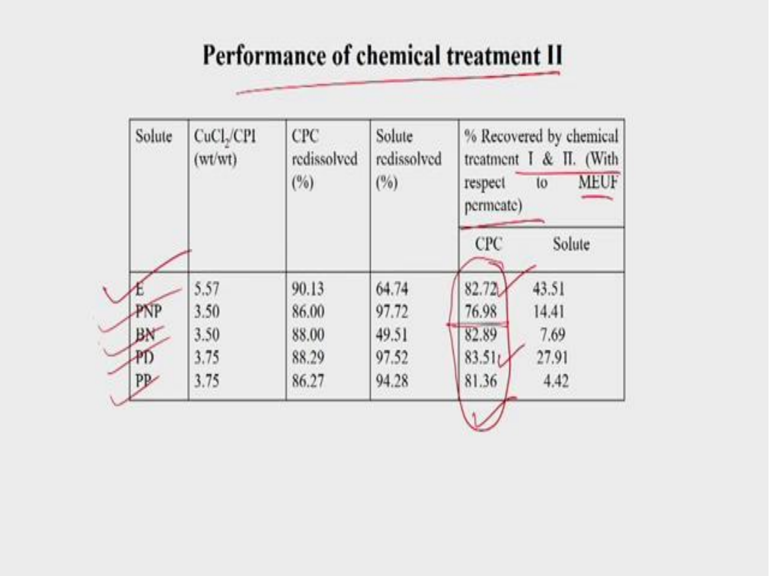

Performance of chemical treatment II

Solute	$CuCl_2/CPI$ (wt/wt)	CPC redissolved (%)	Solute redissolved (%)	% Recovered by chemical treatment I & II. (With respect to MEUF permeate)	
				CPC	Solute
E	5.57	90.13	64.74	82.72	43.51
PNP	3.50	86.00	97.72	76.98	14.41
BN	3.50	88.00	49.51	82.89	7.69
PD	3.75	88.29	97.52	83.51	27.91
PP	3.75	86.27	94.28	81.36	4.42

Whenever will be doing this one in the treatment process two like this regeneration also for this cases for eosin, paranitrophenol, beta naphthol and the potassium dichromate, potassium permanganate. The CPC recovery is to some extends lower like this say it ranges from we can say this it ranges from 77 percent to around 84 percent. So, here actually you see recovery of the by chemical treatment one and two with respect to we can say permeate MEUF permeate it is to some extent lower but overall the we are a able to recover the surfactant which is coming out through this permeate and that can be reused.

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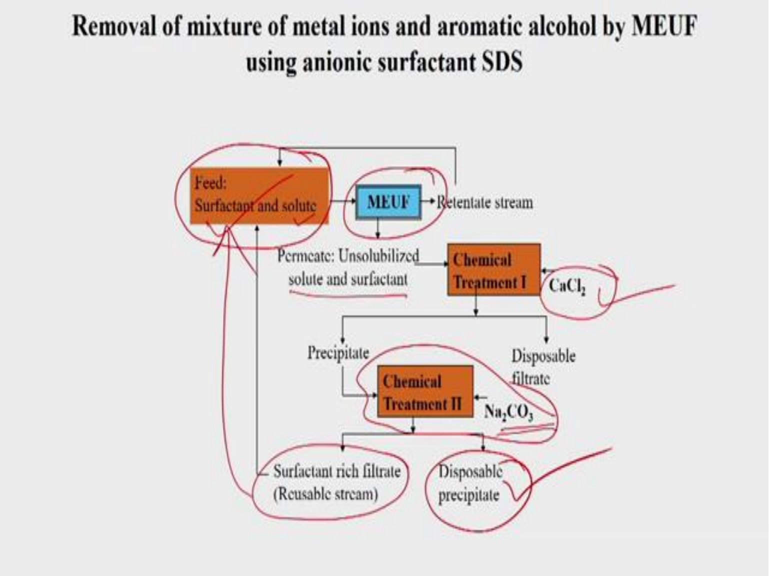
MEUF using anionic surfactant



Removal of mixture of metal ions and aromatic alcohol by MEUF using anionic surfactant SDS

Now, we will be discussing about the MEUF process using this anionic surfactant as almost similarly. Only the difference is that in place of the cationic surfactants or organic (solutants) solutes, now, we will be able to separate these metal ions like this. So, it is the same thing feed contains surfactants as well as the solutes. Then we will be doing the MEUF process. Then whatever the permeate will be there unsolubilized solute and surfactant will be there, will be doing the chemical treatment for the process using this calcium chloride to separate the sodium dodecyl sulphate in terms of calcium dodecyl sulphate.

And it will be precipitated with, then this calcium dodecyl sulphate will be regenerated using sodium carbonate to get the surfactant is filtrate that will be reused for the next MEUF process. And, there will be disposable precipitated this will be discarded.

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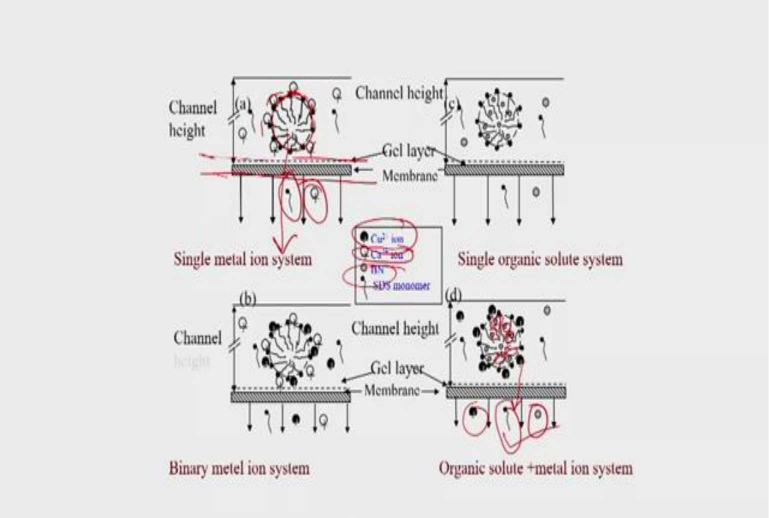

A schematic representation of solubilization of organics and metal ions and filtration by MEUF.

Now, this is the pictorial representation of the separation of the metal ions or organic pollutants like this using these anionic surfactants. Like this the top surface of the anionic say micelle is like this negatively charged. Then we have this suppose this either copper or calcium plus these will be stick on the top surface. This is the membrane surface, then one gel layer will be formed. And, then through this membrane only, water should pass but we told this one that it is not that above CMC.

Some monomers will be there in the surfactants solution so this will be passing through this membrane. And, along with small amount of feed solutes. So, whenever we will be we have this different organic compounds like this beta naphtholate etc. Say this will be trapped inside these globules. And then say after this membrane separation process, some monomers will be coming out and which are not trapped by these globules or which will not be trapped by the micelles will be coming out as the CP.

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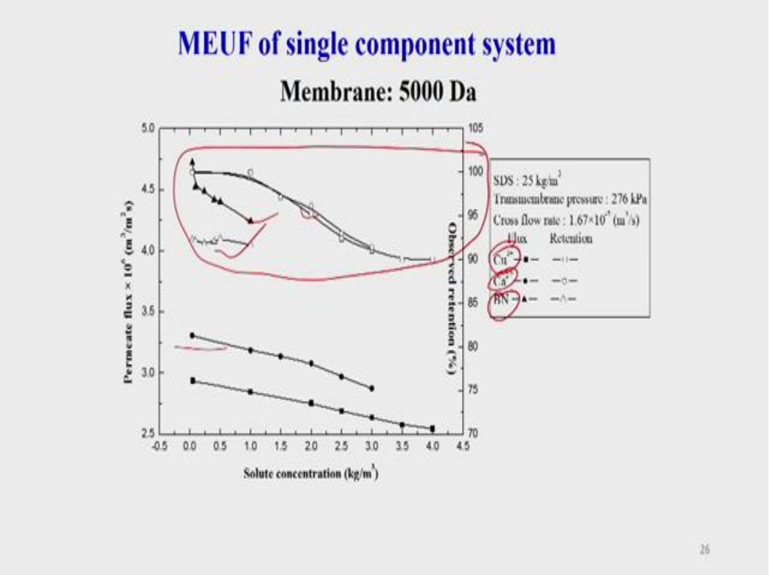

MEUF of single component system

Membrane: 5000 Da

So, here also the schematic representation of the permeate flux value and the retention using this sodium dodecyl sulphate as the 25 kg per meter cube. This is above the CMC and we are assuming that most the monomers are now forming globules and it is able to trap all this copper, calcium and beta naphthol. That is why you see the retention values of all this are always around more than 90 percent for all these cases. But, the flux values are I told earlier also that whenever we have this surfactants solutions then the flux values will be to some extend lower than the actual flux values. So, due to the generation of a small gel layer over the membrane surface.

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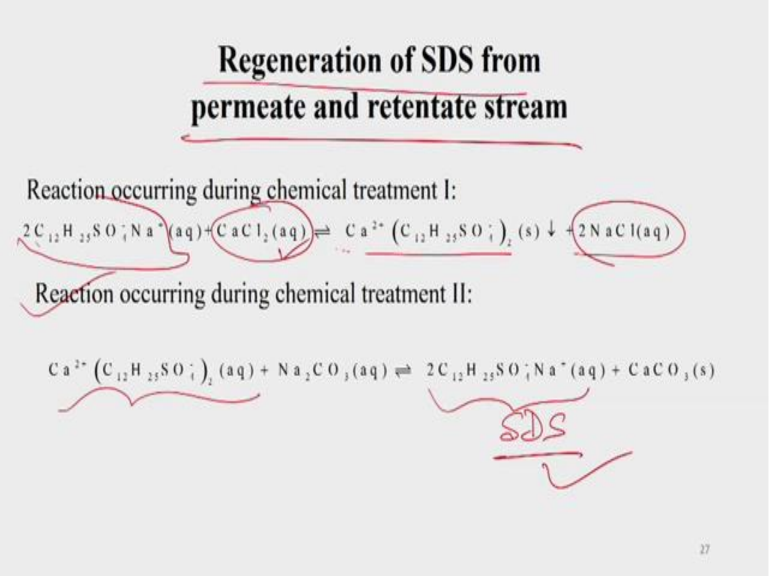

Regeneration of SDS from permeate and retentate stream

Reaction occurring during chemical treatment I:

$$2C_{12}H_{25}SO_4^-Na^+(aq) + CaCl_2(aq) \rightleftharpoons Ca^{2+}(C_{12}H_{25}SO_4^-)_2(s)\downarrow + 2NaCl(aq)$$

Reaction occurring during chemical treatment II:

$$\underbrace{Ca^{2+}(C_{12}H_{25}SO_4^-)_2(aq)} + Na_2CO_3(aq) \rightleftharpoons \underbrace{2C_{12}H_{25}SO_4^-Na^+(aq)}_{SDS} + CaCO_3(s)$$

Now, this regeneration of SDS from permeate and retentate like this. So, this is the SDS and this is calcium chloride in the aqueous solution. Then it will be forming calcium dodecyl sulphate that is you we can say precipitate and sodium chloride will be there in the solution. In the second reaction we can say the second chamber will be converting this calcium dodecyl sulphate into sodium dodecyl sulphate. Which is nothing but the surfactant that will be used for the next process. So, we will be able to separate that this sodium dodecyl sulphate for as in the form of calcium dodecyl sulphate to again sodium dodecyl sulphate.

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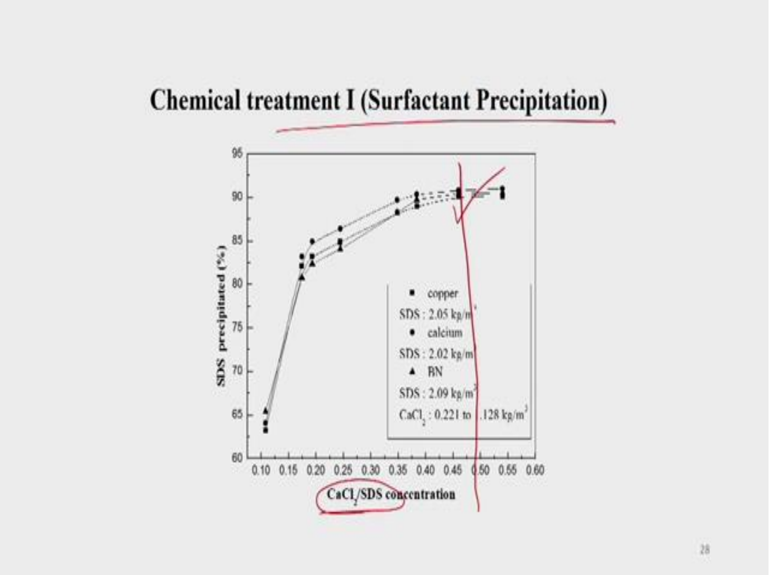
Chemical treatment I (Surfactant Precipitation)



Now, like this is the schematic presentation of chemical treatment one like the surfactant precipitates like this. So, the equation also indicates that the first equation like this 2 moles of surfactants actually reacts with 1 mole calcium chloride. So, here also whenever we this almost 0.5 the ratio between this calcium chloride to SDS it is giving this almost a more than 90 percent SDS precipitation. This is as per the equation or their stoichiometric ratio. So, it is also observed here in presence of the deferent metal ions or also beta naphthol also these organic pollutants.

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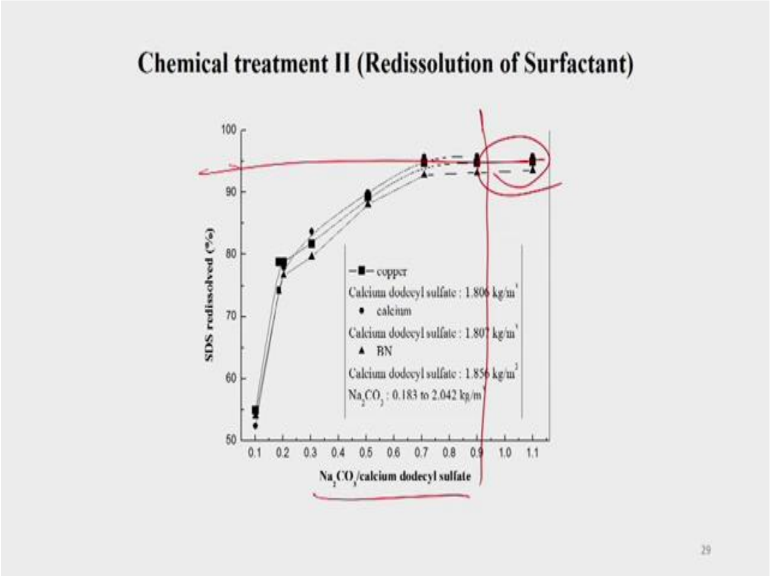

Chemical treatment II (Redissolution of Surfactant)

Because, when the organic pollutants will be there so this will utilize some of the surfactants in the form of these globules. There it will be stick so in for that case we can say the effectiveness or we can say regeneration of the sodium dodecyl sulphate is not 100 percent. Because, some portions remain also in the utilized form with the metal ions. Which is coming out from the through this permeate and that is why here also we have what for almost 1. Because, see is the equation is 1 is to 1 for this one calcium dodecyl sulphate and sodium carbonate this is 1 is to 1. So, it is we can say whenever ratio will be 1 is to 1 so in that case we are due ably able to get almost 95 percent sodium dodecyl sulphate back.

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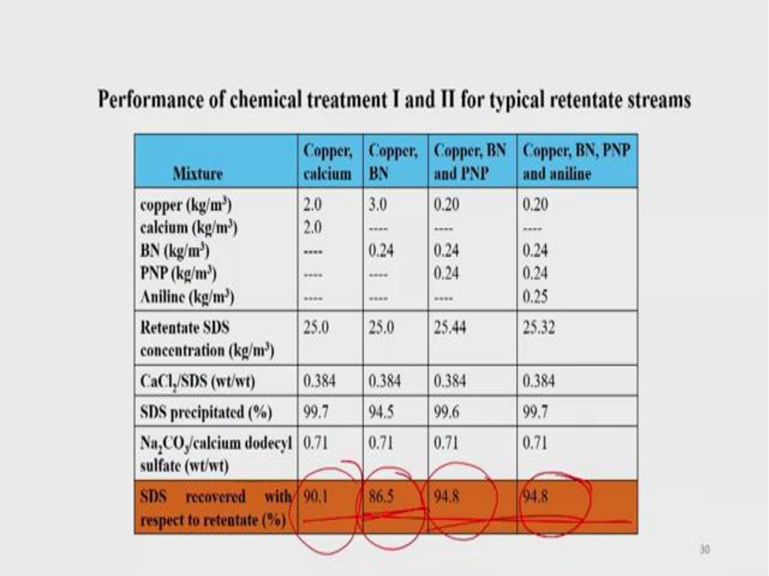

Performance of chemical treatment I and II for typical retentate streams

Mixture	Copper, calcium	Copper, BN	Copper, BN and PNP	Copper, BN, PNP and aniline
copper (kg/m^3)	2.0	3.0	0.20	0.20
calcium (kg/m^3)	2.0	----	----	----
BN (kg/m^3)	----	0.24	0.24	0.24
PNP (kg/m^3)	----	----	0.24	0.24
Aniline (kg/m^3)	----	----	----	0.25
Retentate SDS concentration (kg/m^3)	25.0	25.0	25.44	25.32
$CaCl_2$/SDS (wt/wt)	0.384	0.384	0.384	0.384
SDS precipitated (%)	99.7	94.5	99.6	99.7
Na_2CO_3/calcium dodecyl sulfate (wt/wt)	0.71	0.71	0.71	0.71
SDS recovered with respect to retentate (%)	90.1	86.5	94.8	94.8

So, this are in the tabular form this how much SDS will be recovered for this suppose copper calcium or copper beta naphthol or copper beta naphthol and paranitrophenol mixtures or copper beta naphthol paranitrophenol and aniline. So, in all the cases we have seen that SDS recovery over SDS recovery is around say ranging from 87 to 95 percent. So, that is huge and as we know the cost of this is SDS is very high. So, how much will be able to recover that will be used for the next process and it will increase the economy of the micellar enhanced ultrafiltration process.

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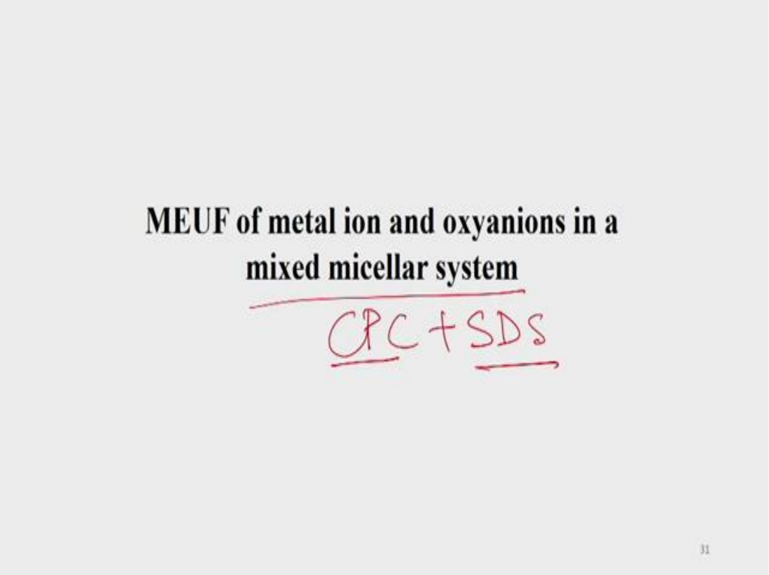

MEUF of metal ion and oxyanions in a mixed micellar system

CPC + SDS

Now, we will be discussing the last topic like this MEUF the metal ion and oxyanions using mixed micellar system like this both CPC and SDS. So, cationic as well as the ionic surfactant mixture. So, we have tested also and we found that the mixed micellar system is effective in separating both the cationic, anionic are surfactants. Because, in this case in mixed micellar system both the cationic moiety and the anionic moieties are present in the system. But, at the same the time throughput of the system actually will go on decreasing as the huge amount of gel layer will be formed over the membrane surface. And, it will give the additional resistance through to the water flux through this membrane.

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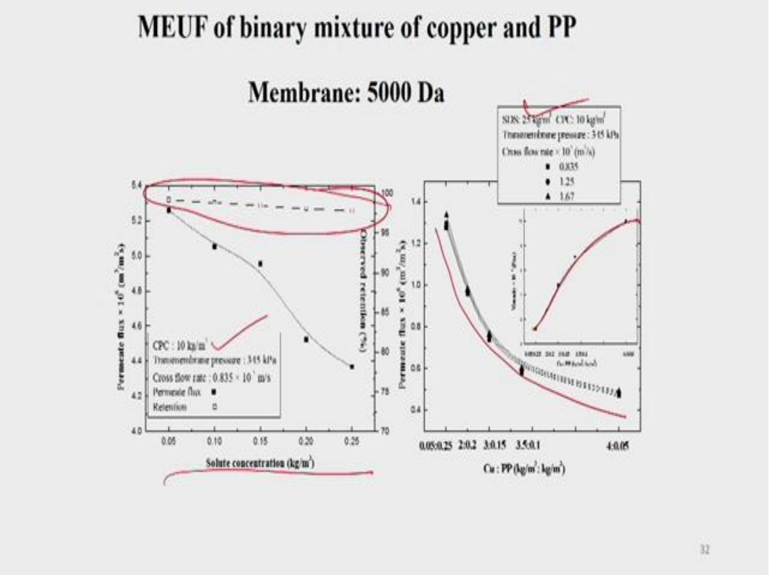

MEUF of binary mixture of copper and PP

Membrane: 5000 Da

Now, we have this CPC concentration it in 10 kg per meter cube and SDS concentration is 25 kg per meter cube. And, in that case whenever we have seen that the observe retention values are almost always more than 97 or 98 percent. But, with the increase of the solute concentration the flux will go on decreasing slowly and slowly. Due to the generation of the gel layer over the membrane surface. And, at the same time permeate flux values that is we can see it is decreasing.

And, viscosity will go on increasing with increase of the solute surfactant concentration in the feed. In this case the membrane was taken as 5000 Dalton. So, the throughput value should be higher than 1000 Dalton membrane because the pore diameter of the 5000 diameter membrane is very high. Or in other words we can say the membrane permeability value of 5000 Dalton membrane is much more than the membrane permeability value of 1000 Dalton membrane.

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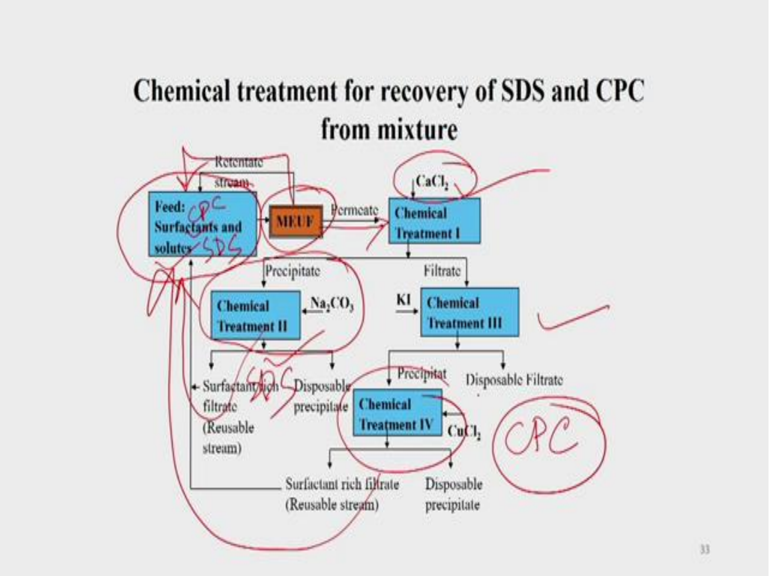

Chemical treatment for recovery of SDS and CPC from mixture

Retentate stream
Feed: Surfactants and solutes
CPC
SDS
MEUF
Permeate
$CaCl_2$
Chemical Treatment I
Precipitate
Filtrate
Chemical Treatment II
Na_2CO_3
KI
Chemical Treatment III
Surfactant rich filtrate (Reusable stream)
Disposable precipitate
SDS
Precipitat
Disposable Filtrate
Chemical Treatment IV
$CuCl_2$
CPC
Surfactant rich filtrate (Reusable stream)
Disposable precipitate

So, now we have these two different surfactants cationic and anionic so we need this 2 different processes for the regeneration. That is why suppose we have this inside this feed we have surfactants and say cationic and anionic CPC and SDS and this all solutes are there. Then through this MEUF process we have 2 different 1 retentate that will coming back to the feed chamber and the permeate will be first treated like this whatever we tested for the separation of say SDS.

Then, we have this precipitate and this filtrate from this whatever the filtrate is there from this we can say chemical treatment III, we will be again we will be doing this chemical treatment IV to get the surfactant treat filtrate and that will be the reused again. Whatever the solubilized form actually we will be getting form chemical treatment II. That will be used again to that membrane separation process. So, first two one or two process will be used to get SDS and this third and fourth will be the regeneration of CPC.

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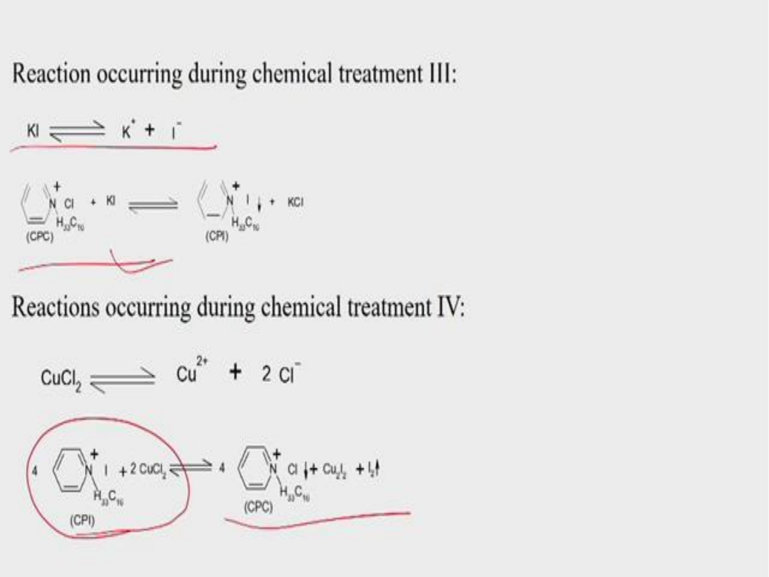

Reaction occurring during chemical treatment III:

$$KI \rightleftharpoons K^+ + I^-$$

Reactions occurring during chemical treatment IV:

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2\,Cl^-$$

So, that is why the process where the first one and two whatever we have discussed this for SDS. Whatever the equation was there same thing for third we can say this potassium iodide will be adding with CPC. And, for whatever the CPI is there we discussed this one at beginning that for cationic surfactant, the same thing is actually we will be doing or reaction 1, 2 will be formed anionic surfactant reaction 3,4 will be for cationic surfactant. And we will be able to get the both the surfactants from different streams. And then we will be reusing the surfactants for the membrane separation process for the mixed micellar system.

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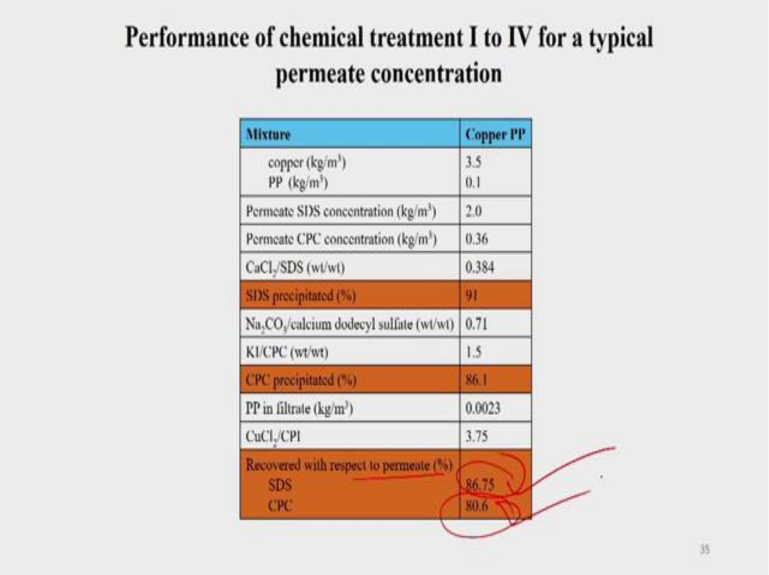

Performance of chemical treatment I to IV for a typical permeate concentration

Mixture	Copper PP
copper (kg/m^3) PP (kg/m^3)	3.5 0.1
Permeate SDS concentration (kg/m^3)	2.0
Permeate CPC concentration (kg/m^3)	0.36
$CaCl_2$/SDS (wt/wt)	0.384
SDS precipitated (%)	91
Na_2CO_3/calcium dodecyl sulfate (wt/wt)	0.71
KI/CPC (wt/wt)	1.5
CPC precipitated (%)	86.1
PP in filtrate (kg/m^3)	0.0023
$CuCl_2$/CPI	3.75
Recovered with respect to permeate (%) SDS CPC	 86.75 80.6

So, this is the performance chemical treatment I to IV and you see one is for SDS overall separation with respect to permeate is 87 percent for CPC it is 81 percent almost. So, we are now able to reuse the surfactants which are coming out through this permeate that will be recycle back to the system for the next process.

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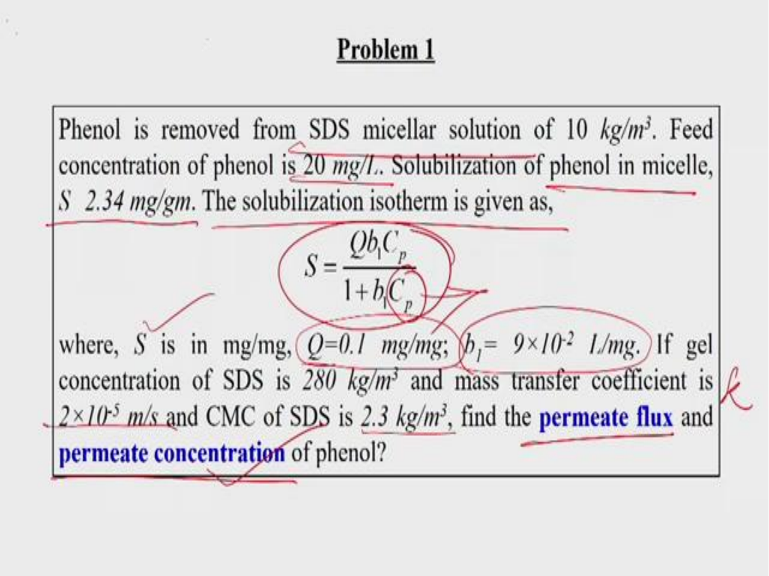

Problem 1

Phenol is removed from SDS micellar solution of 10 kg/m^3. Feed concentration of phenol is 20 mg/L. Solubilization of phenol in micelle, S 2.34 mg/gm. The solubilization isotherm is given as,

$$S = \frac{Qb_1C_p}{1+b_1C_p}$$

where, S is in mg/mg, $Q=0.1$ mg/mg; $b_1 = 9\times10^{-2}$ L/mg. If gel concentration of SDS is 280 kg/m^3 and mass transfer coefficient is 2×10^{-5} m/s and CMC of SDS is 2.3 kg/m^3, find the **permeate flux** and **permeate concentration** of phenol?

Now, we will be solving 1 problem on using this SDS as the micellar solution and this one for that case phenol is the target component. So, phenol is removed from the problem is like that phenol is removed from SDS micellar solution of 10 kg per meter cube. And, feed concentration of the phenol is 20 milligram per liter. Solubilization of the phenol in the micelle is 2.34 milligram per gram of the surfactant. Then solubilization isotherm is given as like land wood type S is equal to q into b1 into Cp by 1 plus b1 into Cp.

That b1 actually is the solubilization constant and q is the solubilization capacity s is isotherm and Cp is the solute concentration of the permeate. So, that Cp is we can say 2.3 kg per meter cube and mass transfer coefficient k that is we can say 2.5 in to 10 to the power minus 5 meter per second. Now, we need to find the permeate flux value and the permeate concentration of the phenol. But, we do not know the solute concentration of the phenol this phenol concentration in the permeate. That we need to find out then we will able to get what is the we can say if know the retention from there we can get the solute concentration in the permeate.

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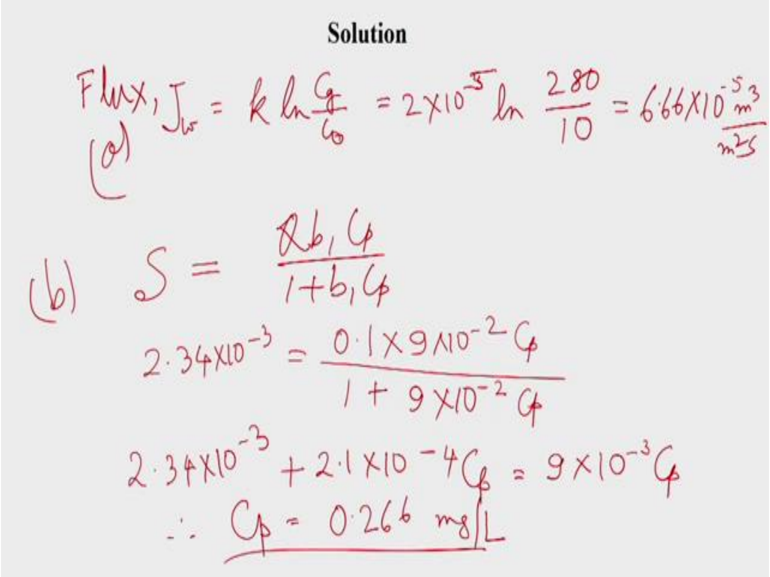

Solution

Flux, (a) $J_w = k \ln \frac{C_g}{C_0} = 2\times10^{-5} \ln \frac{280}{10} = 6.66\times10^{-5} \frac{m^3}{m^2 s}$

(b) $S = \frac{Q b_1 C_p}{1+b_1 C_p}$

$2.34\times10^{-3} = \frac{0.1\times9\times10^{-2} C_p}{1+9\times10^{-2} C_p}$

$2.34\times10^{-3} + 2.1\times10^{-4} C_p = 9\times10^{-3} C_p$

$\therefore \underline{C_p = 0.266 \text{ mg/L}}$

Now, we will be solving this one so here we can say as the this, is we can say it is the gel layer actually is formed. So, gel layer concentration is given so will be using this gel layer theory like this flux. Flux Jw will be equal to k into ln cg by c0 k is given as 2 into 10 to the power minus 5. And ln cg is given as cg 280 kg per meter cube 280 divided by that is c naught is equal to (0) a 10 so it is coming out as flux is coming out as 6.66 into 10 to the power minus 5 say meter cube per square second or meter per second.

So, the first problem is very straight forward for second problem we need to get the concentration of the solute in the permeate. So, for that we have this solubility solubilization isotherm is equal to Q in to b1 into Cp by 1 plus b1 into Cp. So, that solubilization isotherm is given as 2.34 into 10 to the power minus 3 is equal to Q is given 0.1 into 9 into 10 to the power minus 2 into Cp we do not know by 1 plus 9 into 10 to the minus 2 into Cp.

So, then 2.34 into 10 to the power minus 3 plus 2.34 into 9 into 10 to the power minus 3, 10 to the power minus 2 so it will be coming as 2.1 into 10 to the power minus 4 into Cp that will be like this 9 into 10 to the power minus 3 into Cp. Therefore, Cp will be is equal to 0.266 milligram per liter. So, now that is the Cp concentration of the solute or we can say phenol in the permeate. Whatever this permeate concentration of the solute. So, it is this is permeate concentration of the phenol in the permeate.

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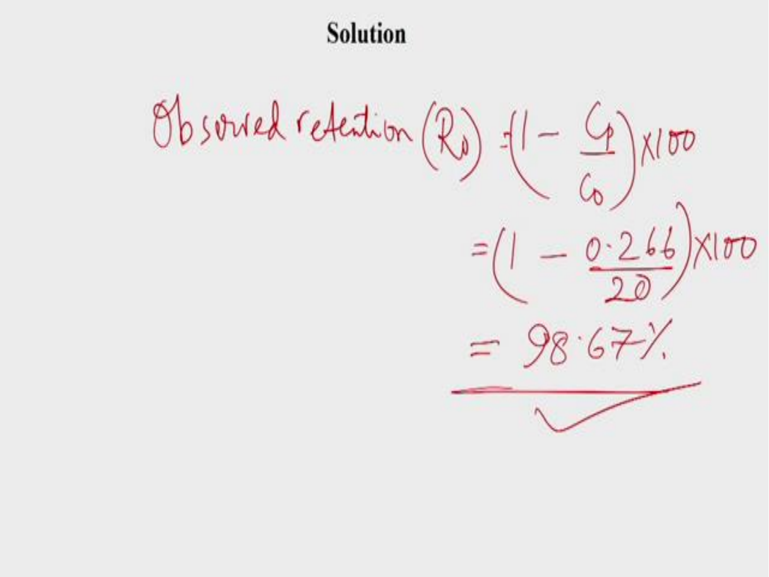

Solution

Observed retention $(R_o) = \left(1 - \frac{C_p}{C_o}\right) \times 100$

$$= \left(1 - \frac{0.266}{20}\right) \times 100$$

$$= 98.67\%$$

So, then from there we can say this is how much retention actually we have. So, we can say we can do observed retention. So, that is Ro is equal to 1 minus Cp by c0 into 100 that is coming out 1 minus 0.266 divide by 20 into 100. So, that is coming out as 98.67 percent so this is we can say the observed retention of the membrane or the observed retention of phenol using this membrane is 98.67 percent.

So, thank you very much so in the next class we will be discussing about absorption and ion exchange.